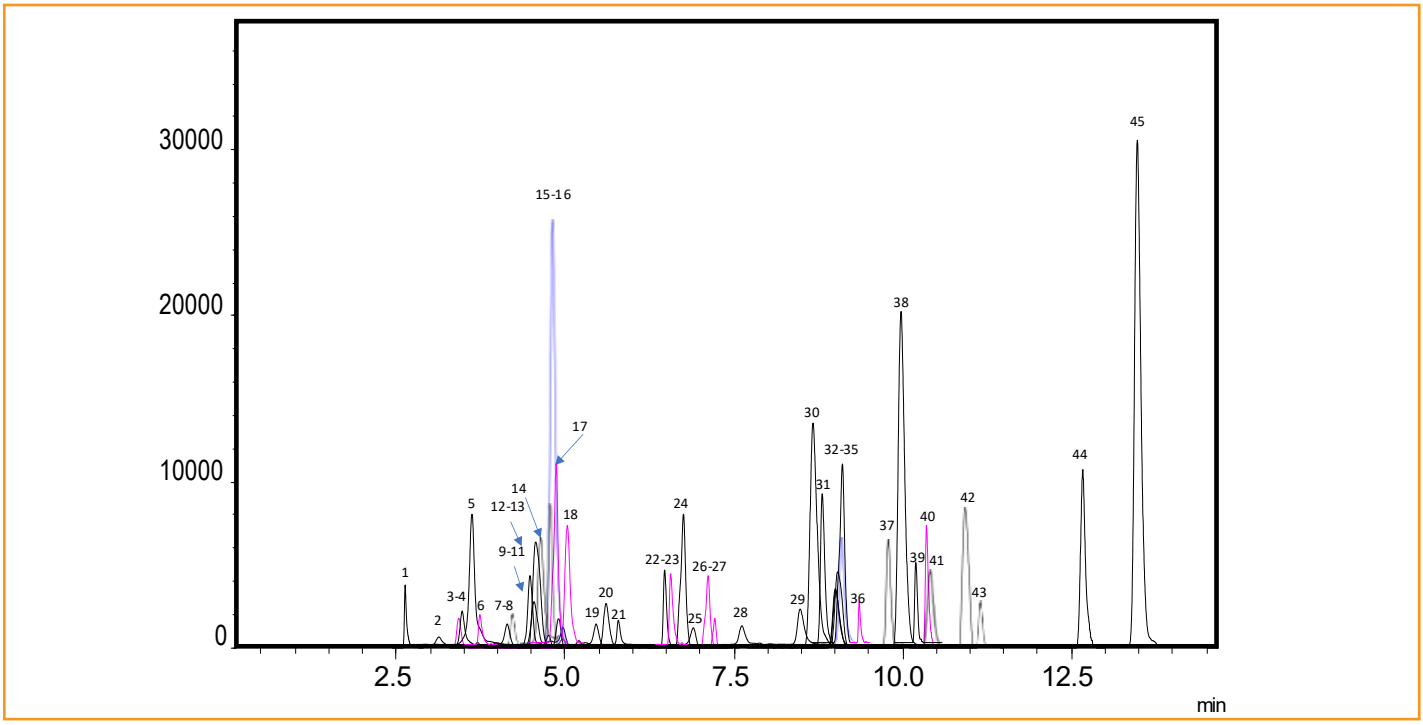
HALO®

PHARMACEUTICALS

LC-MS Analysis of Veterinary Drugs Using HALO® C18

276-vt



TEST CONDITIONS:

Analytical Column: HALO 90 Å C18, 2.7 µm, 2.1 x 100 mm
Part Number: 92812-602
Mobile Phase A: Water, 0.1 % Formic Acid
Mobile Phase B: ACN, 0.1% Formic Acid
Flow Rate: 0.4 mL/min
Pressure: 228 bar
Temperature: 35 °C
Injection Volume: 2.0µL
Sample Solvent: 50/50/ MEOH/H2O
Detection: +ESI MS/MS
LC System: Shimadzu Nexera X2
ESI LCMS system: Shimadzu LCMS-8040
Gradient

Time	%B
0	10
14	100
16	100
16.10	10
19.0	stop

Veterinary drugs are a complex group of substances that can be differentiated into different chemical classes and therapeutic areas. These compounds can further be differentiated based on their classifications, such as macrolides, quinolones, sulfonamides, benzimidazoles, tricyclines, and NSAIDs. Here we present the HALO® C18 for the separation and identification of a complex mix veterinary drugs, including macrolides, quinolones, sulfonamides, benzimidazoles, tricyclines, NSAIDs and 4 dye species which have also been used for therapeutic purposes in veterinary medicine. The high speed separation is easily accomplished and can definitely find application in high throughput environments.

MS Source Conditions:
ESI +
Spray Voltage: 3.0 kV
Nebulizing gas: 2 L/min
Drying gas: 15 L/min
DL temp: 250 ˚C
Heat Block: 400 ˚C

Peak id	Drug	Transition	Reten. Time	Classification
1	Ciprofloxacin	332.1000>314.1000	2.515	Quinolone
2	Sulfathiazole	256.0000>92.0000	3.021	Sulfonamide
3	Lincomycin	407.2000>126.1000	3.334	Lincosamide
4	Sulfapyridine	250.1000>184.0000	3.340	Sulfonamide
5	Albendazole-2amino	240.0000>133.1000	3.582	Benzimidazole
6	Trimethoprim	291.1000>230.0000	3.641	Quinolone
7	Ormetoprim	275.1000>123.1000	4.228	Quinolone
8	Tetracycline	445.1000>410.1000	4.234	Tetracycline
9	Enrofloxacin	360.1000>342.1000	4.520	Quinolones
10	Danofloxacin	358.1000>340.0000	4.532	Quinolones
11	Sulfaclozine	285.0000>156.0000	4.534	Sulfonamide
12	Sulfachloropyridazine	285.0100>92.0000	4.548	Sulfonamide
13	Sulfamerazine	265.0000>108.0000	4.591	Sulfonamide
14	Diclofenac	296.0000>214.0000	4.625	NSAID
15	Difloxacin	400.1000>382.1000	4.941	Quinolone
16	Amoxicillin	366.0000>113.9000	5.015	Beta-lactam
17	Chlortetracycline	479.1000>444.0000	5.027	Tetracyline
18	Sulfadoxine	311.0000>92.0000	5.280	Sulfonamide
19	Sulfaethoxypyridazine	295.0000>140.1000	5.542	Sulfonamide
20	Penicillin G	335.0000>159.9000	5.626	Beta-lactam
21	Neospiramycin	350.2000>174.2000	5.858	Macrolide
22	Spiramycin	422.4000>174.2000	6.521	Macrolide
23	Sulfadimethoxine	311.1000>108.0000	6.527	Sulfonamide
24	Albendazole Sulfoxide	282.1000>208.0000	6.638	Benzimidazole

Peak id	Drug	Transition	Reten. Time	Classification
25	Albendazole Sulfone	298.0000>159.0000	6.669	Benzimidazole
26	Sulfaquinoxaline	301.1000>156.0000	7.027	Sulfonamide
27	Phenylbutazone	309.1000>120.1000	7.106	NSAID
28	Tilmicosin	435.4000>174.1000	7.527	Macrolide
29	Flumequin	262.0000>244.1000	8.508	Quinolone
30	Nalidixic Acid	233.1000>215.1000	8.542	Quinolone
31	Oxolinic Acid	261.9000>244.0000	8.646	Quinolone
32	Kitasamycin	772.3000>174.2000	9.015	Macrolide
33	Tylosin	916.5000>174.1000	9.018	Macrolide
34	Florfenicol Amine	248.0000>230.1000	9.051	Amphenicol
35	Erythromycin A	734.4000>576.4000	9.120	Macrolide
36	Malachite Green	329.2000>313.2000	9.389	Dye
37	Albendazole	266.0000>234.0000	9.829	Benzimidazole
38	Cloxacillin	436.0000>277.0000	10.030	Macrolide
39	Dicloxacillin	470.0000>160.0000	10.080	Macrolide
40	Leucocrystal Violet	374.2000>238.2000	10.360	Dye
41	Crystal Violet	372.2000>356.2000	10.450	Dye
42	Brilliant Green	385.2000>341.1000	11.000	Dye
43	Dapsone	249.0000>156.0000	11.110	Sulfone
44	Carprofen	274.0000>228.1000	12.600	NSAID
45	Ivermectin	897.6000>240.1000	13.140	Macrolide

HALO®

TECHNICAL REPORT

TITLE: **HALO® ENVIROCLASS APPLICATIONS: THE ANALYSIS OF VETERINARY DRUGS, PESTICIDES AND ENVIRONMENTAL CONTAMINANTS**

MARKET SEGMENT: ENVIRONMENTAL

AUTHOR:

Andrew Harron Ph.D., Application Scientist

ABSTRACT

Many challenges exist in environmental and food safety analysis, including the number of potentially carcinogenic compounds that have been reported in our food and water. In the last 20 years, this number has grown significantly, and the nature of these compounds is becoming increasingly more complex. Pharmaceuticals and hormones used in veterinary medicine and animal husbandry and pesticides, are examples of compounds that are commonly found in the environment and food supply, and although regulated, these regulations are subject to revision on a constant basis. In addition, maximum allowable limits are decreasing and emerging environmental contaminants are now leaching into the food supply as well. This will require highly sensitive methods for detection and separation of these compounds for analysis. Here we present how using Fuse-Core® technology enhances this analysis for pesticides, emerging environmental contaminants and veterinary drugs, and can provide detection at limits below regulation.

INTRODUCTION

The scale of agriculture and food production in the United States of America (USA), is truly massive. In the USA, over 37% of the total land mass (or more than 900 million acres) is used for agricultural and livestock farming, and with over 2 million active farms, contributed $1.109 trillion to the U.S. gross domestic product (GDP) in 2019. On average, one farmer can produce enough food to feed over 150 people for the year.[1]

Veterinary drugs and hormones, are a complex group of substances that can be differentiated into various chemical classes and therapeutic areas, such as antivirals, antifungals, and antibiotics. The pharmaceuticals can further be differentiated based on their classifications, such as macrolides, quinolones, sulfonamides, benzimidazoles, tricyclines, and NSAIDs.[2-3] The primary use of the therapeutics is to promote animal growth and maintain good animal health, which lowers the potential of a transmission of a disease from animal to human. However, meat can be contaminated with large quantities of therapeutics as well as steroids, which can lead to many negative health effects for humans. In addition to carcinogenic risks of consuming high levels of hormone infused beef, the use of antibiotics can breed antibiotic-resistant microorganisms in animals, transferable to humans.[2-3]

The use of pesticides is critical for successful crop production, and in turn, the overall economic health of the country. Pesticides are used not only at various stages

KEY WORDS:

Environmental contaminants, veterinary drugs, HALO® Enviroclass

during the crop production cycle, but also during storage, and transportation as well. This creates numerous exposure points for toxic exposure of the residues remaining on vegetables, fruits, grain and cereals, and meats, resulting in negative health and environmental effects.[4-6] Another area of pesticide exposure is bodies of water, usually rivers, resulting from ground water contamination. Upon application to the crops, the pesticides leach into the aquifer and penetrate underground streams. These streams then drain into the rivers, thus providing exposure risks to both humans and animals.[6]

The continued use of the veterinary drugs and pesticides in farming has also led to an increase in the number of environmental contaminants that have proliferated through the food supply as well. Environmental contaminants often result from human waste and contamination, or from naturally occurring sources. One such example of contamination is PFAS. PFAS, a known environmental and water contaminant, has grown to such high levels in animals, plastics, and food packaging, that it can be considered as an emerging food contaminant. In addition, large scale contamination of waterways by pharmaceuticals, is also being detected at alarming levels.

Governmental agencies, including the World Health Organization (WHO), the U.S. Environmental Protection Agency (EPA), and the European Union (EU) have all issued statements to guide on pesticide usage and limits, while the Codex Alimentarius issues statements on the use of veterinary drugs on food-producing animals.[4-8] Maximum residue levels (MRLs), have been established as the highest level that is allowable on foodstuffs, when pesticides or veterinary drugs have been applied. In the United States, these levels are in the PPM range for agricultural products and meat, for tolerated pesticides. In the EU these levels are lower, with the average being 10 ppb for most pesticides except for explicitly prohibited compounds. In the case of veterinary drugs, the EU mandate is in the ppb range as well as the USA.[4-8]

These low levels require analysis that is capable of achieving high sensitivity, to ensure high quality data for meeting MRL requirements in complex food matrices. In addition, it is critical in an evolving situation such as food safety analysis to expect new pesticides, veterinary drugs and environmental contaminants, to be added to the regulations, and imposed limits to be decreased. Therefore, technology must not only meet the demands and regulations of today, but also be able to address the future regulations that will be imposed. Here we present the HALO® Biphenyl and HALO® C18 for the analysis of pesticides and Veterinary drugs, achieving lower levels of detection than stipulated by the EU and US EPA.

EXPERIMENTAL DATA:
Maximum resolution method

Experimental: Pesticides and Environmental contaminants

A Shimadzu LCMS-8040 triple quadrupole mass spectrometer was coupled to a Shimadzu Nexera X2 (Shimadzu Scientific Instruments, USA). Acetonitrile (HPLC grade), Methanol (HPLC grade), water (HPLC grade), formic acid, and ammonium formate were purchased from Millipore Sigma (Burlington, MA).

Samples: Pesticides and Environmental contaminants

Two experiments were performed, the first was a screening of a mixture 191 pesticides, containing both polar and non-polar pesticides to determine the suitability of the column for the analysis. The pesticide mixture was acquired from Millipore Sigma, at a concentration of 5ppm. The second experiment was the analysis of a mixture of environmental contaminants and pesticides that were spiked into egg samples. The pesticides and environmental contaminants were spiked into egg samples, at a concentration of 0.045 ng/mL, and then extracted via QuEChERSER method, and provided by the USDA for the analysis. Briefly, 2 g of sample, using liquid nitrogen, is extracted with 10 mL of 4/1 (v/v) acetonitrile/water for 10 min by shaking, followed by centrifugation for 3 min. A 200 µL portion was transferred to a mini-centrifuge tube and quickly evaporated under nitrogen flow, followed by addition of initial LC mobile phase solvent and ultracentrifuged for 5 min before analysis by LC- (MS/MS).

Column and Gradient: Pesticides and Environmental Contaminants:

Standard mix of 191 pesticides

Analytical Column: HALO 90 Å Biphenyl, 2.7 µm, 2.1 x 100 mm, **Part Number:** 92812-611, **Mobile Phase A**: 5mM ammonium formate, 0.1 % Formic Acid, **Mobile Phase B**: MEOH, 0.1% Formic Acid, 0.4 mL/min. 0-100 %B in 12min. 100 %B 12-16 min, 0 %B 16.10min, 20 End

Spiked Pesticides and Environmental contaminants

Analytical Column: HALO 90 Å Biphenyl, 2.7 µm, 2.1 x 100 mm, Part Number: 92812-611, Mobile Phase A: 5mM ammonium formate, 0.1 % Formic Acid, Mobile Phase B: ACN, 0.1% Formic Acid, 0.4 mL/min. 0-100 %B in 20min. 100 %B 20-22 min, 0 %B 22.10min, 25 End

MS source conditions: Pesticides and Environmental contaminants

Spray Voltage: 3.5 kV Nebulizing gas: 2 L/min Drying gas: 15 L/min DL temp: 250 ˚C Heat Block: 400 ˚C

Experimental: Veterinary Drugs

A Shimadzu LCMS-8040 triple quadrupole mass spectrometer was coupled to a Shimadzu Nexera X2 (Shimadzu Scientific Instruments, USA). Acetonitrile (HPLC grade), water (HPLC grade), formic acid, and ammonium formate were purchased from Millipore Sigma (Burlington, MA).

Samples: Veterinary drugs

The veterinary drugs were spiked into egg samples, at a concentration of 0.045 ng/mL, and then extracted via QuEChERSER method, and provided by the USDA for the analysis. Briefly, 2 g of sample, using liquid nitrogen, is extracted with 10 mL of 4/1 (v/v) acetonitrile/water for 10 min by shaking, followed by centrifugation for 3 min. A 200 µL portion was transferred to a mini-centrifuge tube and quickly evaporated under nitrogen flow, followed by addition of initial LC mobile phase solvent and ultracentrifuged for 5 min before analysis by LC- (MS/MS).

Column and Gradient: Veterinary drugs:

Analytical Column: HALO 90 Å C18, 2.7 µm, 2.1 x 100 mm, **Part Number:** 92812-602, **Mobile Phase A:** Water, 0.1 % Formic Acid, **Mobile Phase B:** ACN, 0.1% Formic Acid, 0.4 mL/min. 10-100% B in 14 minutes. 100-100% B 14-16min, 10% B 16.10 min, 19.0 End

MS source conditions: Veterinary drugs:

Spray Voltage: 3.5 kV Nebulizing gas: 2 L/min Drying gas: 15 L/min DL temp: 275 ˚C Heat Block: 375 ˚C

Results Pesticides and Environmental Contaminants

Previous experimentation had shown the Biphenyl phase's combination of hydrophobic, aromatic, and polar selectivity, provided a fast separation of a pesticide mix consisting of 191 pesticides, showing good retention of both polar and non-polar pesticides. **Figure 1, Table 1** shows the screening of 191 pesticides in less than 16 minutes, and demonstrates the HALO® Biphenyl column to be an excellent choice for high throughput screening for environmental applications.

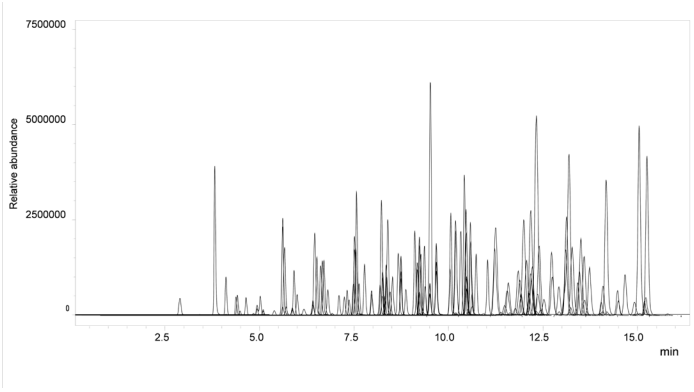


Figure 1. 191 pesticides detected by HALO® Biphenyl
See Table 1 on Page 6

Spiked Samples

Modifications to the gradient, including extending the time, were made to account for the mixture of environmental contaminants that were included in the analysis, and also for any possible unknown matrix effects that could potentially arise. The resulting chromatogram, **Figure 2**, shows the separation of 160 pesticides and environmental contaminants (**Table 2**) in less than 20 minutes.

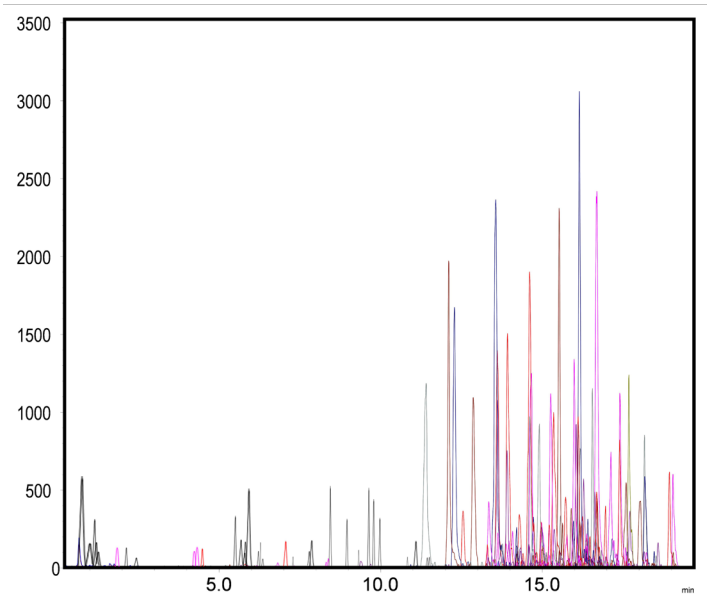


Figure 2. 160 pesticides and environmental contaminants in spiked egg samples

See Table 2 on Page 9

The concentration of the compounds was 0.045 ng/mL, which is significant as it is below the MRL levels established by both the EPA and the EU, demonstrating the sensitivity of the separation, with no matrix effects contributing to ion suppression evident.

Results: Veterinary Drugs

45 veterinary drugs were spiked into egg samples and subjected to QuEChERSER extraction and were obtained from the USDA. A C18 column was chosen for the analysis as it is a universal phase for acids, bases and neutral solutes and has excellent stability at low to mid mobile phase pH, which would provide ample retention for all compounds in the sample. **Figure 3**, shows 45 veterinary drugs detected and classified (**Table 3**) in just over 13 minutes on the HALO® C18. The concentration of the drugs was 0.045 ng/mL, which like the pesticides, is below the MRL recommended by the Codex Alimentarius.

The HALO® C18 enabled the separation and identification of a complex mix of veterinary drugs, including macrolides, quinolones, sulfonamides, benzimidazoles, tetracyclines, NSAIDs and 4 dye species which have also been used for therapeutic purposes in veterinary medicine. The high-speed separation is easily accomplished and can definitely find application in high throughput environments.

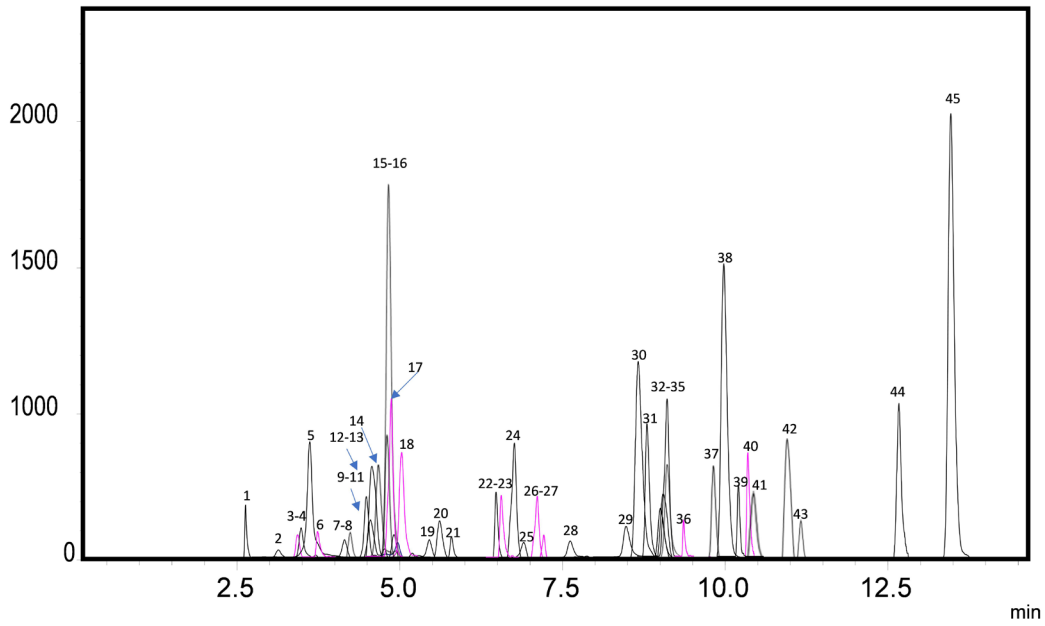


Figure 3. 45 veterinary drugs on HALO® C18
See Table 3 on Page 12

CONCLUSION:

Environmental and food safety analysis can be challenging for a number of reasons, including matrix effects which could lead to ion suppression, incomplete extraction from the various matrices, and difficult separations due to the chemical nature of the compounds. In addition to the current list of challenges, emerging contaminants are sure to add to these challenges and the technology will need to answer those challenges. Coupled with new sample prep technology such as QuEChERSER, HALO® Fused-Core® columns play a critical role in new environmental and food safety analysis workflows, enabling the detection of pesticides and veterinary drugs in food matrices below MRLs established by both the EU and EPA. HALO® columns enable fast, efficient separations covering a full range of compounds for food safety testing, and have the capability to exceed current testing limits, and are well equipped to handle future levels as they arise.

REFERENCES:

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TABLE 1 Pesticides transitions and retention times

Peak number	Name	m/z transition	Ret. Time
1	Cyromazine	167.0000>85.1000	2.894
2	Terbufos sulfone	321.1000>171.0000	3.427
3	Metoxuron	229.1000>72.0500	4.135
4	Propamocarb	189.0000>102.1000	4.530
5	Omethoate	214.0000>125.1000	4.840
6	Monolinuron	215.1000>126.1000	4.841
7	Simetryn	214.0000>124.0000	4.841
8	Butocarboxim sulfoxide	207.1000>75.1000	5.117
9	Butocarboxim	208.1000>75.1000	5.118
10	Aldicarb sulfoxide	207.1000>89.2000	5.119
11	Dinotefuran	203.2500>129.0500	5.157
12	Butoxycarboxim	223.0000>106.2000	5.700
13	Aldoxycarb	240.2000>86.1000	5.787
14	Flonicamid	230.1000>203.0000	5.867
15	Sebuthylazine	229.9000>174.0500	5.868
16	Atrazine-desisopropyl	173.8000>68.1000	6.174
17	Carbendazim	192.1000>160.1000	6.408
18	Pymetrozine	218.1000>105.1000	6.459
19	Oxamyl	237.1000>72.1000	6.721
20	Nitenpyram	271.0000>56.1500	6.747
21	Methomyl	162.8000>106.0000	6.807
22	Oxydemeton-methyl	247.0000>169.0000	6.920
23	Clothianidin	250.1000>132.0000	7.243
24	Demeton-s-methyl sulfone	262.8000>169.0000	7.352
25	Fuberidazole	185.0000>157.0500	7.458
26	Fenuron	164.9000>72.0500	7.505
27	Thiabendazole	202.1000>175.0000	7.547
28	Cyproconazole Isomer	292.0000>70.0000	7.708
29	3-hydroxycarbofuran -21	255.1000>163.1000	7.963
30	Ethidimuron	264.9000>114.0000	8.188
31	Chloridazon	222.1000>104.1000	8.241
32	Ethirimol	210.1000>98.0500	8.363
33	Dioxacarb	224.0000>123.1000	8.392
34	Methiocarb	226.1000>169.1000	8.395
35	Vamidothion	288.0000>146.0500	8.447
36	Cymoxanil	199.1000>128.0000	8.517
37	Ametryn	242.1000>122.1000	8.669
38	Mesurol sulfoxide	242.1000>122.1000	8.669
39	Terbutryn	242.1000>186.1000	8.671
40	Imidacloprid	256.1000>175.0000	8.871
41	Oxycarboxin	268.1000>175.0000	9.137
42	Monuron	199.1000>72.0500	9.170
43	Cycluron	199.1000>72.0500	9.171
44	Methiocarb-sulfone	258.1000>122.1000	9.230
45	Metolcarb	166.1000>109.0000	9.267
46	Thidiazuron	221.1000>102.1000	9.378
47	Diuron	232.8000>72.1000	9.675
48	Fluometuron	233.1000>72.1000	9.677
49	Propoxur	210.1000>111.0000	10.059
50	Fenthion sulfoxide	295.1000>280.0000	10.169
51	Imazamethabenz-methyl	289.1000>144.0000	10.186
52	Myclobutanil	289.0000>70.0000	10.194
53	Bendiocarb	224.1000>109.1000	10.194
54	Chlorotoluron	212.9000>72.0000	10.325
55	Terbumeton	226.1000>170.1000	10.355
56	Propargite	368.3000>231.2000	10.358
57	Pyracarbolid	218.1000>125.1000	10.415
58	Thiacloprid	253.0000>126.0500	10.462
59	Forchlorfenuron	248.1000>129.0000	10.473
60	Methabenzthiazuron	222.1000>165.2000	10.488
61	Carbofuran	222.2000>165.1000	10.489

Peak number	Name	m/z transition	Ret. Time
62	Quinoclamine	208.0000>89.0000	10.515
63	Isoprocarb	194.1000>95.0000	10.576
64	Carbaryl	202.1000>145.1000	10.589
65	Metobromuron	259.0000>148.0500	10.623
66	Benoxacor	260.0000>149.1000	10.630
67	Buturon	237.1000>84.1000	10.731
68	Isoproturon	207.0000>72.1500	10.747
69	Sulfentrazone	387.0000>309.0000	10.789
70	Ethiofencarb	226.0000>107.1000	10.831
71	Naptalam	292.1000>144.1000	10.875
72	Thiobencarb	258.0000>125.0000	10.894
73	Tepraloxydim	342.2000>250.1500	10.963
74	Spiroxamine	298.0000>144.1500	11.083
75	Carboxin	236.0000>143.0500	11.087
76	Tebuthiuron	229.1000>172.4000	11.090
77	Fenpropimorph	304.2000>147.1000	11.266
78	Linuron	249.0000>159.9500	11.276
79	Fenobucarb	208.0000>95.1000	11.304
80	Siduron	233.3000>94.0000	11.377
81	Penconazole	284.1000>70.0000	11.393
82	Ethiprole	396.9500>350.8500	11.402
83	Ethoxyquin	218.0000>174.0500	11.452
84	Desmedipham	318.0000>182.5000	11.496
85	1-Dodecylguanidine	228.1000>71.1000	11.517
86	Phenmedipham	318.1000>168.0000	11.602
87	Disulfoton sulfoxide	291.0000>213.0000	11.612
88	Halofenozide	331.1000>105.0000	11.636
89	Azamethiphos	325.0000>183.0000	11.636
90	Promecarb	208.1000>109.0000	11.753
91	Thifensulfuron-methyl	388.1000>167.1000	11.798
92	Diethofencarb	268.2000>226.1000	11.802
93	Tridemorph	298.1000>130.1000	11.814
94	Flurtamone	334.1000>247.0500	11.950
95	Tebufenpyrad	334.0000>145.0000	11.950
96	Fenthion sulfone	311.0000>109.0000	11.956
97	Cyprodinil	226.0000>93.0000	11.960
98	Pencycuron	329.2000>125.1000	11.961
99	Fomesafen	456.1000>344.0000	12.044
100	Iprovalicarb	321.2000>119.2000	12.131
101	Flutolanil	324.1000>242.0000	12.154
102	Chlorantriniliprole	484.1000>452.9000	12.251
103	Trinexapac-ethyl	253.2000>69.0000	12.252
104	Neburon	275.1000>88.1000	12.257
105	Isoxaflutole	360.1000>251.1000	12.308
106	Benalaxyl	326.2000>294.1000	12.316
107	Chloroxuron	291.1000>72.1000	12.407
108	Dimethametryn	256.1000>186.0500	12.409
109	Fenazaquin	307.1000>161.0000	12.439
110	Terbufos-sulfoxide	305.1000>186.8000	12.444
111	Ethofumesate	287.1000>258.9000	12.449
112	Fenamidone	312.1000>92.1000	12.493
113	Clethodim	360.0000>164.0500	12.528
114	Piperonyl butoxide	356.2000>177.2000	12.554
115	Boscalid	343.0000>307.0000	12.568
116	Methoxyfenozide	369.2000>149.0000	12.585
117	Bioresmethrin	339.2000>171.0500	12.619
118	Hydramethylnon	495.2000>323.2000	12.632
119	Rimsulfuron	432.1000>182.0000	12.698
120	Fenchlorphos oxon	304.9000>109.0000	12.699
121	Tralkoxydim	330.2000>284.1500	12.720
122	Epoxiconazole	330.1000>121.1000	12.721
123	Ipconazole Isomer	334.2000>70.0000	12.827
124	Thiofanox	219.2000>57.2000	12.834
125	Fenbuconazole	337.0000>124.9000	12.909
126	Zoxamide	336.1000>187.0000	12.910
127	Benthiazole	239.0000>179.9500	12.922
128	Isoxaben	333.2000>165.0000	13.019
129	Metconazole	320.2000>70.0500	13.032
130	Triflumuron	359.1000>156.0000	13.057
131	Mandipropamid	412.2000>328.1500	13.071

Peak number	Name	m/z transition	Ret. Time
132	Isoprothiolane	291.0000>230.9500	13.084
133	Acibenzolar-s-methyl	210.9000>136.0000	13.166
134	Cyflufenamid	413.2000>295.1000	13.247
135	Dimethomorph	388.2000>301.1000	13.266
136	Flutriafol	302.1000>70.1000	13.278
137	Fenoxycarb	302.2000>116.0000	13.284
138	Spirotetramat	374.3000>302.1500	13.301
139	Novaluron	491.1000>471.1000	13.308
140	Fluquinconazole	376.1000>349.0500	13.393
141	Spinosad (Spinosyn A)	732.5000>142.2000	13.430
142	Bensulfuron-methyl	411.2000>149.1000	13.439
143	Cyazofamid	325.1000>108.0000	13.485
144	Carfentrazone-ethyl	412.1000>346.0000	13.515
145	Pinoxaden	401.2000>317.2000	13.527
146	Picoxystrobin	368.1000>145.0000	13.570
147	Pyraflufen-ethyl	413.1000>339.0000	13.610
148	Phoxim	299.0000>77.1000	13.632
149	Fenothiocarb	254.1000>72.1000	13.634
150	Mefenacet	298.9000>148.0500	13.636
151	Triflusulfuron-methyl	493.2000>264.1000	13.659
152	Azoxystrobin	404.2000>372.1000	13.724
153	Hexaflumuron	462.8000>158.1000	13.726
154	Chlorimuron-ethyl	415.1000>186.0000	13.746
155	Haloxyfop-methyl	376.0500>316.0000	13.769
156	Lufenuron	509.0000>339.0000	13.782
157	Metaflumizone	507.2000>178.0000	13.788
158	Kresoxim-methyl	313.9500>267.3000	13.844
159	Anilofos	368.2000>125.0000	13.963
160	Tetraconazole	372.1000>159.0000	13.964
161	Sethoxydim	328.1000>296.3000	14.062
162	Famoxadone	392.0000>331.1000	14.078
163	Teflubenzuron	381.1000>141.2000	14.082
164	Clofentezine	303.0000>138.0000	14.122
165	Haloxyfop-etotyl	434.0500>315.9000	14.186
166	Trifloxystrobin	409.1000>186.1000	14.197
167	Pretilachlor	312.0000>252.1000	14.237
168	Diflubenzuron	328.0000>141.0000	14.265
169	Diclobutrazol	328.2000>70.2000	14.266
170	Fluoxastrobin	459.1000>427.1000	14.287
171	Flufenoxuron	489.1000>158.1000	14.374
172	Metrafenone	409.1000>209.0500	14.403
173	Piperophos	354.1000>170.9000	14.425
174	Fenoxaprop-ethyl	362.1000>288.1000	14.475
175	Pyraclostrobin	390.1000>194.1000	14.483
176	Benzoximate	364.0000>199.0000	14.560
177	Diniconazole	326.2000>70.2000	14.633
178	Isocarbophos	307.0000>121.1000	14.721
179	Spiromesifen	371.3000>273.2000	14.724
180	Chlorfluazuron	540.1000>383.0000	14.744
181	Chlorthiophos	360.7500>304.9000	14.761
182	Furathiocarb	383.2000>195.1000	14.772
183	Pyriproxyfen	322.0000>96.0000	14.821
184	Chinomethionate	235.0000>207.0500	14.833
185	Spirodiclofen	411.2000>71.1000	15.001
186	Propaquizafop	444.2000>100.1000	15.117
187	Avermectin B1a.	890.5000>567.5000	15.265
188	Rotenone	395.2000>213.1000	15.267
189	Fenpyroximate	422.3000>366.2000	15.339
190	Cyphenothrin	376.2000>181.0000	15.351
191	Phenothrin	351.2000>183.0000	15.423

TABLE 2 Pesticides and Environmental Contaminants Trasnitions and Retention Times

ID#	Name	m/z	Ret. Time
1	Mercapto -Methylimidazole	114.8800>57.1000	0.449
2	Dimetridazole hydroxy	158.0000>140.1000	0.544
3	Diuron	232.9400>72.0000	0.557
4	Daminozide	161.0100>143.0000	0.669
5	Ketoprofen	255.1000>77.0000	0.729
6	Propanil	218.0000>162.1000	0.921
7	Nalidixic Acid	233.1000>215.1000	1.095
8	Methamidophos	141.9000>94.0000	1.739
9	Methomyl	163.0200>106.0000	2.163
10	Niflumic Acid	283.0000>265.0000	2.441
11	Acephate	184.0000>143.1000	2.515
12	Aldicarb sulfoxide	207.0200>132.1000	4.269
13	Dinotefuran	203.0600>129.1000	4.376
14	Omethoate	214.0000>182.9000	4.552
15	Quinclorac	241.9000>224.0000	5.051
16	Flonicamid	230.0200>203.1000	5.758
17	Aldicarb sulfone	223.0200>86.1000	5.812
18	Salbutamol	240.2000>148.1000	5.842
19	Ipronidazole hydroxy	186.0000>168.0000	6.089
20	Pymetrozine	217.9900>104.9000	6.104
21	Carbendazim	192.0000>160.1000	6.219
22	Flunixin	297.0000>279.0000	6.641
23	Nitenpyram	271.0000>126.0000	6.969
24	OxamylNH4	237.0100>72.0000	7.051
25	Oxydemeton Methyl	246.9300>169.1000	7.348
26	Clothianidin	250.0000>169.2000	7.705
27	AldicarbNH4	208.1000>116.1000	7.821
28	Ciprofloxacin	332.1000>314.1000	8.318
29	Dicrotophos	238.0000>112.0000	8.371
30	Thiamethoxam	292.0100>211.1000	8.426
31	Dimethoate	229.9500>199.1000	8.843
32	Cymoxanil	199.0000>128.1000	9.295
33	SulfoxaflorNH4	294.9700>174.1000	9.396
34	Atrazine	216.0300>174.1000	9.398
35	Meclofenamic Acid	296.0000>278.0000	9.681
36	Imidacloprid	255.9400>209.0000	9.987
37	Xylazine	221.0000>164.0000	10.047
38	Mercapto benzimidazole	150.9600>93.0000	10.399
39	Dichlorvos	220.9000>109.0000	10.762
40	Acetamiprid	223.0100>126.0000	10.948
41	Cyprodinil	226.0500>93.1000	11.113
42	Tebuthiuron	229.0000>172.3000	11.389
43	Morantel	221.1000>123.0000	11.395
44	Imazethapyr	290.0200>245.1000	11.445
45	Trimethoprim	291.1000>230.0000	11.467
46	Diflufenzopyr	335.0000>206.2000	11.574
47	Metalaxyl	280.0100>220.2000	11.796
48	Carbofuran	222.0000>123.0000	12.106
49	Thiacloprid	252.9800>126.2000	12.282
50	Imazalil	296.9700>159.1000	12.551
51	Albendazole Sulfone	298.0000>159.0000	12.561
52	Fenbufen	255.1000>181.1000	12.675
53	Flunixin-d3	300.0000>282.0000	12.785
54	Thiophanate Methyl	343.0200>151.0000	12.871
55	C-lencyclohexerol	319.1000>301.0000	12.986
56	Propyphenazone	231.1000>189.1000	13.135
57	Linuron	248.9000>160.1000	13.304
58	2-Aminoflubendazole	256.0000>123.0000	13.347
59	Fenobucarb	208.0500>95.0000	13.355
60	Fosthiazate	283.9800>228.0000	13.513
61	Dodemorph	282.2000>116.1000	13.556
62	Azamethiphos	324.9000>183.0000	13.613
63	Ethiprole	398.9000>352.9000	13.626
64	EthiproleNH4	413.9000>351.0000	13.641
65	Pronamide	256.0000>190.0000	13.716

ID#	Name	m/z	Ret. Time
66	Pyrimethanil	200.1000>107.2000	13.739
67	Paclobutrazol	294.0300>70.0000	13.914
68	Norflurazon	303.9000>284.0000	13.936
69	Cyantraniliprole	475.1000>286.0000	13.956
70	Triadimenol	296.0000>70.1000	14.074
71	Methiocarb	226.0100>169.0000	14.209
72	Etoxazole	360.1700>141.0000	14.222
73	Chlorsulfuron	357.9000>167.1000	14.234
74	Triasulfuron	401.9800>167.0000	14.299
75	Fenthion Sulfone	311.0000>125.0000	14.328
76	Mabuterol	311.1000>237.0000	14.576
77	Fluxapyroxad	382.0000>362.1000	14.591
78	Iprovalicarb	321.1000>119.0000	14.611
79	Fluopyram	396.9800>208.0000	14.619
80	Flutolanil	324.0000>242.1000	14.652
81	Chlorantraniliprole	484.0000>452.9000	14.715
82	Fenhexamid	302.0600>96.9000	14.732
83	Myclobuthanil	289.0100>70.0000	14.903
84	Penthiopyrad	360.0400>276.1000	14.961
85	Tetraconazole	372.0000>159.1000	14.987
86	Fenamidone	312.0000>236.2000	15.003
87	Saflufenacil	501.0000>349.0000	15.014
88	Boscalid	343.0000>307.1000	15.092
89	Clethodim	360.0000>164.0000	15.123
90	Ethoprophos	243.0600>172.9000	15.222
91	Methidathion	302.8800>144.9000	15.233
92	Methoxyfenozide	369.1000>149.1000	15.266
93	Fenarimol	330.9000>268.1000	15.309
94	Hexaconazole	315.9900>69.9000	15.353
95	Thiodicarb	354.9600>88.0000	15.361
96	Tebuconazole	308.0200>70.0000	15.375
97	Fenoterol	304.1000>107.2000	15.491
98	Fenamiphos	304.0000>217.1000	15.524
99	Diflubenzuron	310.9600>158.0000	15.536
100	Penconazole	285.9500>70.0000	15.568
101	Flufenacet	363.9500>194.1000	15.582
102	Bifenazate	301.1000>198.1000	15.726
103	Penoxsulam	484.0000>195.2000	15.758
104	Benzovindiflupyr	398.0500>342.0000	15.897
105	Flusilazole	315.9900>247.0000	15.965
106	Epoxiconazole	330.0000>121.1000	15.991
107	Dimethomorph	388.0600>301.0000	16.048
108	Phosmet	318.0100>160.0000	16.114
109	Fenoxycarb	302.0000>116.0000	16.145
110	Triazophos	313.9200>162.0000	16.152
111	Spirotetramat	374.1200>302.1000	16.161
112	Diazinon	305.0000>169.1000	16.176
113	Spiromesifen	388.1100>273.2000	16.237
114	Fenbuconazole	337.0200>125.0000	16.238
115	Bitertanol	338.1100>269.1000	16.367
116	Cyazofamid	324.9000>107.9000	16.372
117	Tolylfluanid	347.0000>137.0000	16.377
118	Novaluron	493.0100>158.2000	16.396
119	Tetrachlorvinphos	364.9000>127.0000	16.414
120	Triflumizole	346.0500>277.9000	16.473
121	Chlorfenvinphos	358.9000>155.1000	16.476
122	Isofenphos	346.0100>245.1000	16.531
123	Phorate	260.9300>74.9000	16.554
124	Picoxystrobin	368.0000>145.1000	16.556
125	Propiconazole	342.0700>159.1000	16.564
126	Pyraflufen Ethyl	412.9000>339.0000	16.633
127	Pirimiphos Methyl	305.9000>164.2000	16.686
128	Azoxystrobin	404.0400>372.1000	16.686
129	Chlorimuron Ethyl	414.9680>186.0000	16.699
130	Disulfoton	274.9500>88.9000	16.834
131	Fenthion	279.0000>247.0000	16.838
132	Tebufenpyrad	334.0900>145.1000	16.954
133	Prallethrin	301.0500>123.1000	16.975

ID#	Name	m/z	Ret. Time
134	Spinetoram	748.4000>142.2000	17.118
135	Prochloraz	375.9000>308.2000	17.16
136	Profenofos	372.9000>302.8000	17.162
137	Chlorpyriphos Methyl	321.9000>125.0000	17.206
138	Clofentezine	303.0000>138.0000	17.322
139	Fluoxastrobin	459.0000>427.0000	17.396
140	Trifloxystrobin	409.1000>186.1000	17.411
141	Malachite Green leuco	331.2000>239.1000	17.577
142	Difenoconazole	406.0000>250.9000	17.584
143	Phosalone	367.9000>182.1000	17.631
144	Piperonyl Butoxide	356.1100>177.2000	17.687
145	Pyraclostrobin	388.1000>194.2000	17.699
146	Fenoxaprop Ethyl	361.9800>288.0000	17.716
147	Indoxacarb	527.9000>248.8000	17.751
148	Quizalofop Ethyl	373.0000>299.1000	18.024
149	Crystal Violet leuco	374.2000>238.2000	18.168
150	Pyriproxyfen	322.0600>95.9000	18.172
151	Pyrazophos	374.0100>222.0000	18.186
152	Coumaphos	362.8000>227.0000	18.217
153	PropargiteNH4	368.1000>231.2000	18.245
154	Hexythiazox	353.0100>228.1000	18.431
155	Spirodiclofen	411.1000>313.0000	18.463
156	Acequinocyl	357.2000>329.3000	18.521
157	Fenpropathrin NH4	367.1100>125.0000	18.586
158	Fenpyroximate	422.2000>366.1000	18.934
159	Phenothrin	351.0800>183.0000	19.048
160	Pyridaben	365.0500>309.0000	19.054

TABLE 3 Veterinary Drugs Transition Times and Retention Times

Peak id	Drug	Transition	Retention Time	Classification
1	Ciprofloxacin	332.1000>314.1000	2.515	Quinolones
2	Sulfathiazole	256.0000>92.0000	3.021	Benzimidazoles
3	Lincomycin	407.2000>126.1000	3.334	Quinolones
4	Sulfa pyridine	250.1000>184.0000	3.341	Sulfonamide
5	Albendazole-2-amino	240.0000>133.1000	3.582	Benzimidazoles
6	Trimethoprim	291.1000>230.0000	3.641	Quinolones
7	Ormetoprim	275.1000>123.1000	4.228	Quinolones
8	Tetracycline	445.1000>410.1000	4.234	Tetracycline
9	Enrofloxacin	360.1000>342.1000	4.524	Quinolones
10	Danofloxacin	358.1000>340.0000	4.532	Quinolones
11	Sulfaclozine	285.0000>156.0000	4.534	Sulfonamide
12	Sulfachloropyridazine	285.0100>92.0000	4.548	Sulfonamide
13	Sulfamerazine	265.0000>108.0000	4.591	Sulfonamide
14	Diclofenac	296.0000>214.0000	4.625	NSAID
15	Difloxacin	400.1000>382.1000	4.941	Quinolones
16	Amoxicillin	366.0000>113.9000	5.015	Macrolide
17	Chlortetracycline	479.1000>444.0000	5.027	Tetracyline
18	Sulfadoxine	311.0000>92.0000	5.283	Sulfonamide
19	Sulfaethoxypyridazine	295.0000>140.1000	5.542	Sulfonamide
20	Penicillin G	335.0000>159.9000	5.626	Macrolide
21	Neospiramycin 2H	350.2000>174.2000	5.858	Macrolide
22	Spiramycin	422.4000>174.2000	6.521	Macrolide
23	Sulfadimethoxine	311.1000>108.0000	6.527	Sulfonamide
24	Albendozole Sulfoxide	282.1000>208.0000	6.638	Benzimidazoles
25	Albendazole Sulfone	298.0000>159.0000	6.669	Benzimidazoles
26	Sulfaquinoxaline	301.1000>156.0000	7.027	Sulfonamide
27	Phenylbutazone	309.1000>120.1000	7.106	NSAID
28	Tilmicosin	435.4000>174.1000	7.527	Macrolide
29	Flumequin	262.0000>244.1000	8.508	Quinolones
30	Nalidixic Acid	233.1000>215.1000	8.542	Quinolones
31	Oxolinic Acid	261.9000>244.0000	8.646	Quinolones
32	Kitasamycin	772.3000>174.2000	9.015	Macrolide
33	Tylosin	916.5000>174.1000	9.018	Macrolide
34	Florfenicol Amine	248.0000>230.1000	9.051	Sulfonamide
35	Erythromycin A	734.4000>576.4000	9.122	Macrolide
36	Malachite Green	329.2000>313.2000	9.389	Dye
37	Albendazole	266.0000>234.0000	9.829	Benzimidazoles
38	Cloxacillin	436.0000>277.0000	10.031	Macrolide
39	Dicloxacillin	470.0000>160.0000	10.081	Macrolide
40	Crystal Violet leuco	374.2000>238.2000	10.363	Dye
41	Crystal violet	372.2000>356.2000	10.452	Dye
42	Brilliant Green	385.2000>341.1000	11.001	Dye
43	Dapsone	249.0000>156.0000	11.110	Sulfonamide
44	Carprofen	274.0000>228.1000	12.602	NSAID
45	Ivermectin	897.6000>240.1000	13.142	Macrolide